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(54) **Semiconductive ceramic and semiconductive ceramic element using the same**

Halbleitende Keramik und halbleitendes keramisches Element damit

Céramique semiconductrice et élément céramique semiconducteur l'utilisant

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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a semiconductive ceramic, more specifically to a semiconductive ceramic having negative resistance-temperature characteristics. The present invention also relates to a semiconductive ceramic element making use of the semiconductive ceramic.

10 Background Art

[0002] Semiconductive ceramic elements having high resistance at ambient temperature and negative resistance-temperature ("NTC") characteristics by which resistance decreases with increase of temperature (such an element having NTC characteristics hereinafter called an "NTC element") are known. Through utilization of the NTC characteristics, the NTC element has been used for various purposes such as the suppression of rush current, retarding starting of a motor, and protection of halogen lamps.

[0003] For example, a NTC element rush current device suppresses overcurrent by absorbing the initial rush current, so as to prevent destruction of a halogen lamp or a semiconductive element such as an IC or diode due to overcurrent flowing through a circuit upon the switching-on of the power, and to prevent a decrease in service life of such a component. Thereafter, the NTC element reaches high temperature through self-heating so that its resistance decreases and, in a steady state, power consumption is reduced accordingly.

[0004] When current is passed through a motor for a gear mechanism - the motor being designed to be fed with a lubricating oil after starting of the motor - so as to rotate the gears immediately at a high rotational speed, the gears may be damaged due to insufficient supply of the lubricating oil. Also, in a lapping machine which grinds the surface of a ceramic through rotation of a grinding stone, the ceramic may be cracked when the lapping machine is rotated at a high rotational speed upon starting of the drive motor. In order to avoid these problems, the terminal voltage of the motor is lowered by means of an NTC element, so as to retard the starting of the motor. Thereafter, the NTC element comes to have lowered resistance through self-heating, so that the motor runs normally in a steady state.

[0005] As a semiconductive ceramic having NTC characteristics and constituting these NTC elements, there has been used spinel composite oxides containing a transition metal element such as Mn, Co, Ni or Cu.

[0006] Lanthanum cobalt oxides have been reported to have NTC characteristics such that the B constant has temperature dependency; that is, the B constant increases with increase of temperature (V. G. Bhide and D. S. Rajoria *at al.* Phys. Rev. B6, [3], 1072, 1972, etc.).

[0007] When an NTC element is used for suppression of rush current, it must have a decreased resistance at the elevated temperature caused by self-heating. However the conventional semiconductive ceramic using spinel composite oxide usually has a tendency that the B constant decreases as resistance decreases. Therefore, at an elevated temperature the resistance cannot be sufficiently lowered, with the result that power consumption is not reduced in a steady state.

[0008] Also, in a conventional semiconductive ceramic, resistance increases considerably at low temperatures below 0°C, resulting in a voltage drop which retards the start-up of an apparatus or machine.

[0009] A conventional semiconductive ceramic element making use of conventional lanthanum cobalt oxide has a B constant of as high as 6000 K at an elevated temperature. However, since it has a B constant of 4000 K or more at low temperature, when used as an NTC element for suppression of rush current, the apparatus or machine to which the element is incorporated suffers a considerable voltage drop at low temperature.

[0010] CH. ZOCK et al.: J. of magnetism and magnetic materials, Vol. 150, No. 2, 1995, pages 253-262, XP000529027 discloses $\text{La}_{1-z}\text{Ca}_z\text{CoO}_3$ while V. GOLOVANOW: Physical Review B, condensed matter, Vol., 53, No. 13, 1 April 1996, pages 8207-8210, XP000594202 and R.N. SINGH: J. Chem. Soc., Faraday Trans., Vol. 92, No. 14, 1996, pages 2593-2598, XP000597952 q disclose $\text{La}_{1-z}\text{Sr}_z\text{CoO}_3$.

50 SUMMARY OF THE INVENTION

[0011] Accordingly, an object of the present invention is to provide a semiconductive ceramic in which the B constant is maintained at about 4000 K or more at elevated temperature to thereby decrease power consumption, and the B constant is lowered at sufficiently low temperature so as to increase resistance more than required to thereby prevent a voltage drop in an apparatus or machine.

[0012] This object is achieved with a semiconductive ceramic having the features of claim 1. The subclaims are directed to preferable embodiments.

[0013] Another object of the present invention is to provide a semiconductive ceramic element using the semiconductive ceramic. This object is achieved with a semiconductive ceramic element having the features of claim 7.

[0014] With a composition of the inventive semiconductive ceramic, the B constant is maintained above about 4000 K at an elevated temperature, and thus the resistance of the semiconductive ceramic is lowered, leading to a reduction in power consumption. At low temperature, on the other hand, the B constant becomes sufficiently lower so that the resistance of the semiconductive ceramic increases to a proper level as to prevent an overcurrent from flowing through an apparatus or machine, to thereby prevent unnecessary retarding of start-up of the apparatus or machine.

[0015] By substituting a portion of La with at least one element selected from among Pr, Nd and Sm there can be obtained a semiconductive ceramic having excellent NTC characteristics.

[0016] Preferably, the semiconductive ceramic contains the oxide serving as a secondary component in an amount of about 0.001-1 mol% calculated as the element. Through incorporation of the secondary component(s) in such an amount, the B constant is 4000 K or lower at low temperature, to thereby more effectively mitigate a drastic increase in resistance of the semiconductive ceramic.

[0017] Preferably, the aforementioned lanthanum cobalt oxide is La_xCoO_3 ($0.5 \leq x \leq 0.999$). With this composition, there can be obtained a semiconductive ceramic having excellent NTC characteristics.

[0018] The preferred uses of the semiconductive ceramic element of the present invention encompass suppression of rush current, retarding of starting of a motor, protection of halogen lamps, and use as a temperature-compensated crystal oscillator. When used in such applications, the characteristics of the semiconductive ceramic element of the present invention are more fully exploited.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

[0019] Now will be described a process for manufacturing the semiconductive ceramic of the present invention and a semiconductive ceramic element using the ceramic.

[0020] First, La_xCoO_3 and Co_3O_4 were provided as starting materials and weighed so as to adjust the mole ratio of lanthanum to cobalt as desired, to thereby obtain a powder. According to the invention, some portion of the La is substituted with a rare earth metal such as Pr, Nd or Sm. Subsequently, at least one element selected from the group consisting of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ni, Cu and Zn was weighed to a predetermined amount in the form of, for example, an oxide, and incorporated into the powder, to thereby obtain an additive.

[0021] The thus-obtained additive was wet-mixed along with pure water and nylon balls for 24 hours, followed by drying. The resultant mixture was calcined at 900-1200°C for two hours, to thereby obtain a calcined material.

[0022] Next, the calcined material was mixed with a binder and nylon balls. The mixture was subjected to filtration, drying, and then press-forming into a disk shape, to thereby obtain a compact

[0023] The compact was calcined at 1200-1600°C for two hours in air, to thereby obtain a semiconductive ceramic.

[0024] Subsequently, a silver-palladium paste was applied onto both surfaces of the semiconductive ceramic, and the semiconductive ceramic was baked at 800-1200°C for five hours to form external electrodes, to thereby obtain a semiconductive ceramic element.

[0025] Tables 1 to 3 and the corresponding description are incorporated in order to assist in understanding the invention. Inventive examples are described with respect to table 4.

[0026] According to the above-mentioned method, there were manufactured semiconductive ceramic elements containing lanthanum cobalt oxide ($\text{La}_{0.94}\text{CoO}_3$) as the primary component, and different types and amounts of secondary components. The resistivity and B constant of each semiconductive ceramic element were measured. The results are shown in Table 1. Data from semiconductive ceramic elements in which a plurality of oxides were employed as secondary components are shown in Table 2. In the Tables, "o" represents good characteristics with no problems in practical use, and "Δ" represents somewhat poor characteristics but no problems in practical use.

[0027] Resistivity (ρ) was measured at 25°C. B constant represents the change of resistance induced by the change of temperature and is defined by the following equation, wherein resistivity $\rho(T)$ is the resistivity at temperature T, resistivity $\rho(T_0)$ is the resistivity at temperature T_0 , and \ln is natural logarithm.

$$B \text{ constant} = \{\ln\rho(T_0) - \ln\rho(T)\} / (1/T_0 - 1/T)$$

[0028] As the B constant increases, there is an increase in the change of resistance induced by the change of temperature. According to this equation, the B constants determined in Example 1, i.e. B(-10°C) and B(140°C), are defined as follows:

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$$B(-10^{\circ}\text{C}) = \frac{\ln\rho(-10^{\circ}\text{C}) - \ln\rho(25^{\circ}\text{C})}{\frac{1}{10+273.15} - \frac{1}{25+273.15}}$$

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Table 1

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Sample No.	Added element		Resistivity	B constant		Evaluation
	Species	Amount (mol%)	ρ 25°C ($\Omega\cdot\text{cm}$)	B(-10°C) (K)	B(140°C) (K)	
1	Ca	0.0001	15.7	4360	6010	Δ
2	Ca	0.0005	14.8	4170	5800	Δ
3	Ca	0.001	14.1	3950	5570	O
4	Ca	0.005	13.3	3800	5320	O
5	Ca	0.01	12.6	3760	5130	O
6	Ca	0.05	11.9	3680	4880	O
7	Ca	0.1	11.4	3460	4570	O
8	Ca	0.5	10.8	3330	4270	O
9	Ca	1	9.9	3090	4060	O
10	Ca	2	7.7	2700	3800	Δ
11	Li	0.1	11.7	3510	4590	O
12	Na	0.1	11.7	3500	4590	O
13	K	0.1	11.6	3500	4590	O
14	Rb	0.1	11.4	3470	4570	O
15	Cs	0.1	11.5	3480	4570	O
16	Be	0.1	11.4	3460	4580	O
17	Mg	0.1	11.5	3470	4580	O
18	Sr	0.1	11.5	3470	4580	O
19	Ba	0.1	11.4	3460	4580	O
20	Ni	0.1	11.5	3470	4590	O
21	Cu	0.1	12	3460	4570	O
22	Zn	0.1	11	3460	4570	O
Comparative example	-	0	17	4410	6270	-

Table 2

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Sample No.	Added element		Resistivity	B constant		Evaluation
	Species	Amount (mol%)	ρ 25°C ($\Omega\cdot\text{cm}$)	B(-10°C) (K)	B(140°C) (K)	
23	Na	0.001	14.0	3920	5500	O
	Mg	0.0005				
24	K	0.005	13.1	3790	5260	O
	Zn	0.001				

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Table 2 (continued)

Sample No.	Added element		Resistivity	B constant		Evaluation
	Species	Amount (mol%)	ρ 25°C ($\Omega\cdot\text{cm}$)	B(-10°C) (K)	B(140°C) (K)	
25	Cu	0.01	12.0	3730	5090	O
	Ni	0.01				
26	Ba	1.0	8.9	2780	3940	Δ
	Zn	0.5				
27	Ca	0.05	11.3	3430	4480	O
	Ba	0.05				
	Li	0.05				
28	Sr	0.1	10.3	3220	4100	O
	Ni	0.1				
	Mg	0.5				

In the semiconductive ceramic elements containing $\text{La}_{0.94}\text{CoO}_3$ as the primary component and at least one oxide of an element selected from the group consisting of Li, Na, K; Rb, Cs, Be, Mg, Ca, Sr, Ba, Ni, Cu and Zn as a secondary component, as shown in Table 1, the B constant is decreased at low temperature, while the B constant is maintained above 4000 K at high temperature.

[0029] Moreover, as shown in Table 2, even in the case where a plurality of oxides are used as the secondary components, if the total amount thereof falls within the range from about 0.001 to 1 mol%, the B constant is decreased at low temperature, while the B constant is maintained above 4000 K at high temperature.

[0030] The reasons why the above-mentioned range provides advantages are as follows.

[0031] The amount of the secondary component(s) is restricted to about 0.001 mol% to 1 mol% because when the amount of the secondary component(s) is less than about 0.001 mol% as in the case of Sample Nos. 1 and 2, the B constant disadvantageously exceeds 4000 K at low temperature, whereas when the amount of the secondary component(s) is more than about 1 mol%, the B constant disadvantageously falls below 4000 K at high temperature.

[0032] In manner similar to the above description semiconductive elements were manufactured by changing the amount x of lanthanum with respect to that of cobalt in lanthanum cobalt oxide La_xCoO_3 serving as the primary component while fixing the secondary component to Ca and the amount of the secondary component to 0.01 mol%. The resistivity and B constant of each semiconductive ceramic element were measured. The results are shown in Table 3. Similarly, the results obtained by use of $\text{La}_x\text{M}_y\text{CoO}_3$ (M represents at least one species selected from among Pr, Nd and Sm), which is lanthanum cobalt oxide serving as the primary component of which lanthanum is partially substituted with another element, are shown in Table 4. In this case, the amount of La (i.e., x) was fixed to 0.85, and the amount of substituting element(s) (i.e., y) was fixed to 0.09. In the Tables, "O" represents good characteristics with no problems in practical use, " Δ " represents somewhat poor characteristics but no problems in practical use, and "X" represents problems in practical use.

Table 3

Sample No.	Amount of La	Added element		Resistivity	B constant		Evaluation
	x (mol)	Species	Amount (mol%)	ρ 25°C ($\Omega\cdot\text{cm}$)	B(-10°C) (K)	B(140°C) (K)	
40	0.4	Ca	0.01	78.1	2680	3870	Δ
41	0.5	Ca	0.01	40.5	3070	4120	O
42	0.7	Ca	0.01	29.3	3460	4690	O
43	0.90	Ca	0.01	12.8	3740	5110	O
44	0.999	Ca	0.01	13.7	3700	5020	O
45	1	Ca	0.01	21.5	3650	4940	X

Table 4

Sample No.	Amount of La	Substituting element		Added element		Resistivity	B constant		Evaluation
	x (mol)	Species	Amount y (mol)	Species	Amount (mol%)	ρ 25°C ($\Omega \cdot \text{cm}$)	B(-10°C) (K)	B(140°C) (K)	
46	0.85	Pr	0.09	Ca	0.005	13.5	3830	5350	O
47	0.85	Nd	0.09	Ca	0.05	12.0	3700	4880	O
48	0.85	Sm	0.09	Ca	0.5	10.9	3350	4290	O
49	0.85	Pr Nd	0.03 0.06	Ca	0.001	14.3	3960	5570	O
50	0.85	Nd Sm	0.01 0.08	Ca	0.01	12.7	3770	5150	O
51	0.85	Pr Nd Sm	0.03 0.03 0.03	Ca	0.1	11.4	3480	4580	O

[0033] As shown in Table 3, when the amount of lanthanum, x, with respect to 1 mol of cobalt contained in the primary component falls in the range of about 0.5 - 0.999 mol, the B constant at low temperature can be reduced to less than 4000 K while B constant at high temperature is maintained at 4000 K or more.

[0034] As shown in Table 4, inventive samples in which lanthanum is partially substituted with at least one of Pr, Nd and Sm in the above-specified amount range have a B constant at low temperature be reduced to a lower value while the B constant at high temperature is maintained at about 4000 K or more.

[0035] The amount of lanthanum, x, is limited to about 0.5-0.999, since, as in the case of sample No. 40, the B constant at high temperature disadvantageously becomes 4000 or less when the amount of lanthanum, x, is less than 0.5. In contrast, as in the case of sample No. 45 having an amount of lanthanum of more than 0.999, the B constant satisfies the conditions of the present invention both at high temperature and low temperature. However, unreacted lanthanum oxide (La_2O_3) contained in a sintered piece of semiconductive ceramic reacts with moisture in air to result in expansion and breaking of the ceramic, which is disadvantageous for use as the element of the present invention.

[0036] As described hereinabove, the semiconductive ceramic of the present invention contains lanthanum cobalt oxide as a primary component and at least one oxide selected from the group consisting of oxides of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ni, Cu or Zn as a secondary component, and thus obtains NTC characteristics by which the B constant is maintained at 4000 K or more at high temperature, while the B constant at low temperature is further decreased.

[0037] Therefore, the semiconductive ceramic enables manufacture of an excellent semiconductive ceramic element (NTC thermistor element) which has low resistance at high temperature leading to lowered power consumption, and prevents an excessive voltage drop in an apparatus or machine at low temperature.

[0038] That is, the thus-obtained semiconductive ceramic element can be widely used as an element for retarding of starting of a motor, protection of the drum of a laser printer, protection of bulbs such as halogen lamps, and elimination of rush current occurring in an apparatus or machine in which an excess current flows at the initial stage of voltage application as well as rush current occurring in a switching power, and also can be used as a temperature-compensated element for TCXO as well as that for general use, and as a temperature detection element.

Claims

1. A semiconductive ceramic comprising (a) a La_xCoO_3 as the primary component, and (b) at least one oxide of an element selected from the group consisting of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ni, Cu and Zn, wherein a portion of the La of the La_xCoO_3 is replaced by at least one element selected from the group consisting of Pr, Nd and Sm.
2. A semiconductive ceramic according to Claim 1, wherein the (b) oxide is in an amount of about 0.001-1 mol% calculated as said element thereof.
3. A semiconductive ceramic according to Claim 2, wherein $0.5 \leq x \leq 0.999$.
4. A semiconductive ceramic according to Claim 2, containing an oxide of Ca or Cu.
5. A semiconductive ceramic according to Claim 2, containing 2 or 3 of said (b) oxides.
6. A semiconductive ceramic according to Claim 2, wherein the (b) oxide is in an amount of about 0.005 - 0.9 mol% calculated as said element thereof.
7. A semiconductive ceramic element comprising a semiconductive ceramic of one of the claims 1 to 6 and an electrode on said ceramic.
8. A rush current suppressor containing a semiconductive ceramic element according to Claim 7.
9. A device for retarding the starting of a motor containing a semiconductive ceramic element according to Claim 7.
10. A device for the protection of halogen lamps containing a semiconductive ceramic element according to Claim 7.
11. A temperature-compensated crystal oscillator containing a semiconductive ceramic element according to Claim 7.

Patentansprüche

1. Keramischer Halbleiter, umfassend (a) ein La_xCoO_3 als der Hauptkomponente, und (b) mindestens ein Oxid eines Elements, gewählt aus der Gruppe, bestehend aus Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ni, Cu und Zn,
 wobei ein Teil des La aus La_xCoO_3 durch mindestens ein Element ersetzt ist, gewählt aus der Gruppe, bestehend aus Pr, Nd und Sm.
2. Keramischer Halbleiter nach Anspruch 1, wobei das (b) Oxid in einer Menge von etwa 0,001-1 Mol-%, berechnet als das Element davon, vorliegt.
3. Keramischer Halbleiter nach Anspruch 2, wobei $0,5 \leq x \leq 0,999$.
4. Keramischer Halbleiter nach Anspruch 2, enthaltend ein Oxid von Ca oder Cu.
5. Keramischer Halbleiter nach Anspruch 2, enthaltend 2 oder 3 der (b) Oxide.
6. Keramischer Halbleiter nach Anspruch 2, wobei das (b) Oxid in einer Menge von etwa 0,005-0,9 Mol-%, berechnet als das Element davon, vorliegt.
7. Keramisches Halbleiter-Element, umfassend einen keramischen Halbleiter nach einem der Ansprüche 1 bis 6 und eine Elektrode auf diesem Keramikum.
8. Stromspitzenausgleich, enthaltend ein keramisches Halbleiter-Element nach Anspruch 7.
9. Element zur Startverzögerung eines Motors, enthaltend ein keramisches Halbleiter-Element nach Anspruch 7.
10. Element zum Schutz von Halogenlampen, enthaltend ein keramisches Halbleiter-Element nach Anspruch 7.
11. Temperatur-kompensierter Kristalloszillator, enthaltend ein keramisches Halbleiter-Element nach Anspruch 7.

Revendications

1. Céramique semiconductrice comprenant (a) La_xCoO_3 comme composant principal et (b) au moins un oxyde d'un élément choisi dans le groupe comprenant Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ni, Cu et Zn, où une partie du lanthane de La_xCoO_3 est remplacée par au moins un élément choisi dans le groupe comprenant Pr, Nd et Sm.
2. Céramique semiconductrice selon la revendication 1, où l'oxyde (b) est présent en une quantité d'environ 0,001 à 1 mol % calculée au titre dudit élément de celui-ci.
3. Céramique semiconductrice selon la revendication 2, où $0,5 \leq x \leq 0,999$.
4. Céramique semiconductrice selon la revendication 2, contenant un oxyde de Ca ou de Cu.
5. Céramique semiconductrice selon la revendication 2, contenant deux ou trois desdits oxydes (b).
6. Céramique semiconductrice selon la revendication 2, où l'oxyde (b) est présent en une quantité d'environ 0,005 à 0,9 mol %, calculée au titre dudit élément de celui-ci.
7. Élément en céramique semiconductrice comprenant une céramique semiconductrice telle que définie dans l'une quelconque des revendications 1 à 6, ainsi qu'une électrode présente sur ladite céramique.
8. Suppresseur de courant d'appel contenant un élément en céramique semiconductrice défini dans la revendication 7.
9. Dispositif permettant de retarder le démarrage d'un moteur contenant un élément en céramique semiconductrice défini dans la revendication 7.

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10. Dispositif destiné à protéger des lampes à halogènes contenant un élément en céramique semiconductrice défini dans la revendication 7.

5 **11.** Oscillateur à cristal à compensation de température contenant un élément en céramique semiconductrice défini dans la revendication 7.

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